Mercury in Novelty and Children's Products made with Polyvinyl Chloride or Polyurethane

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Overview

In 2015, the Washington State Department of Ecology (Ecology) performed a study to evaluate the presence of mercury in novelty and children's products made with polyvinyl chloride (PVC) and polyurethane (PU).

The study was conducted to help Ecology assess compliance with Washington State's Mercury Law (Chapter 70.95 Revised Code of Washington (RCW)) and the Children's Safe Products Act (CSPA; Chapter 70.240 RCW). The Mercury Law prohibits the sale of mercury-added novelty products. By law, novelty items are defined as products intended for personal or household enjoyment of adornment. CSPA further requires manufacturers of children's products report on the presence of Chemicals of High Concern to Children (CHCC), including mercury (> 0.5 ppm).

Baby block letter toy with polyurethane foam inside material.

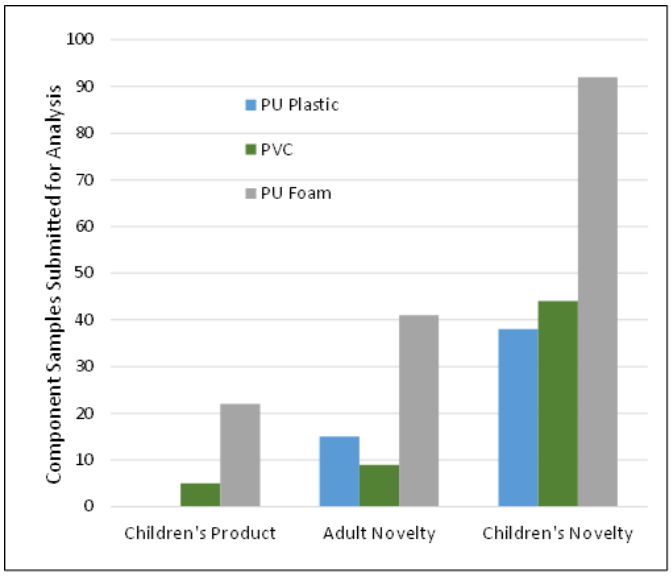

Figure 1. Product Component Samples Submitted for Laboratory Analysis Sorted by Product Matrix and Product Demographic Category.

Ecology purchased 266 products made from PVC or polyurethane. The products were broken down into individual components. PVC and polyurethane components were screened with an X-ray fluorescence (XRF) instrument for the presence of mercury. The XRF screening also confirmed products were likely made of PVC due to high levels (~15%) of chlorine.

A total of 266 components were selected as samples for laboratory analysis (Figure 1).

Mercury was detected in 30 of these 266 component samples, with concentrations ranging from 0.010 to 0.520 ppm.

[1]"Mercury-added" as defined in the law: when mercury or a mercury compound is intentionally added to provide a specific characteristic, appearance, or quality, or to perform a specific function, or for any other reason.

For More Information

Ecology's Mercury website: http://www.ecy.wa.gov/mercury/

Ecology's Children's Safe Products Act website: http://www.ecy.wa.gov/programs/hwtr/RTT/cspa/index.html

List of Chemicals of High Concern to Children: http://www.ecy.wa.gov/programs/hwtr/RTT/cspa/chcc.html

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Methods

Product Collection, Laboratory Sample Selection and Sample Processing

During April of 2015, Ecology purchased 266 PVC or polyurethane novelty products intended for use by both adults and children. These products were purchased from 25 Puget Sound retail stores and 3 online retailers. The practice of purchasing from large retail stores, with statewide distribution, helps to ensure that purchases reflect products sold across the state. Products purchased from large online retailers fits within the standard purchasing approach as online retailers are considered accessible by most state residents. Several additional products purchased from a children's museum retail store were presumed to be similar to those stocked at other children's specialty retail and museum shops located throughout Washington. One other product component sample was collected from both the Chemicals of High Concern to Children in Clothing, Footwear and Accessories (Mathieu, 2015) and the Toxics and Packaging 2014 –2015 (van Bergen, 2014) study. Both products met the study sample requirements and purchasing strategy of this study (i.e., a children's novelty product made of polyurethane).

This study focused on three categories of products, which were derived from the Mercury Law and CSPA. The categories, as described in the Quality Assurance Project Plan (QAPP), were: adult novelty, children's novelty, and children's-only products (Sekerak, 2015). Products made from PVC, or PU, in the form of foams and plastics, were targeted (Table 1). For the purposes of this study, polyurethane products were limited to those made of foams and plastics. Products containing polyurethane adhesives/binders and coatings were not evaluated, although it is possible some products contained polyurethane adhesives/binders.

Table 1. Targeted and Acquired Products by Category.

	PVC			Polyurethane(PU) foam or plastic			
	Adult Novelty	Children's Novelty	Children's Products	Adult Novelty	Children's Novelty	Children's Products	Total Number of Samples
Targeted	5	34	5	56	111	55	266
Acquired	10	45	5	55	129	22	266

Purchased products were cataloged in Ecology's Product Testing Database and separated into 349 individual product components. To aid in sample selection for laboratory analyses, each component was screened for mercury and chlorine with an XRF analyzer. Individual manufacturer product labels describing the product or product components' material composition helped to determine products made from PU or PVC, and PVC was confirmed with XRF screenings of chlorine. Screening for mercury with the XRF did not produce any valid mercury detections for this study. This was mainly because the low levels (as later determined by laboratory analysis) of mercury in the products were below the minimum limit of detection (LOD; 10 ppm) of the XRF analyzer. The low density of the foams and the thin plastics presented additional difficulties in the quantification of mercury (Thermo, 2011).

Laboratory Preparation Method Study

Due to the lack of widely accepted laboratory methodology for the preparation of consumer products for contaminant analysis, a pre-treatment and preparation method study was conducted prior to the main study. Two product matrices (PVC and PU foam) were used in the method study evaluation. Five product samples were submitted for each of the matrix types.

Separately, the five PVC matrix samples and five PU foam matrix samples (Figure 1) were each divided into two

sample portions. The first portion was cryomilled, while the other was snipped into 2 mm x 2 mm pieces. Each cryomilled portion and each snipped portion were then further divided in half before undergoing the preparation method step.

All of the portions were then subjected to one of two microwave-assisted preparation methods based upon EPA Method 3052 modified (less hydrofluoric acid). Each method regime consisted of a slight variation in acid amounts, sequence of acid additions, and microwave (heat and pressure) set-ups, as described in the project plan.

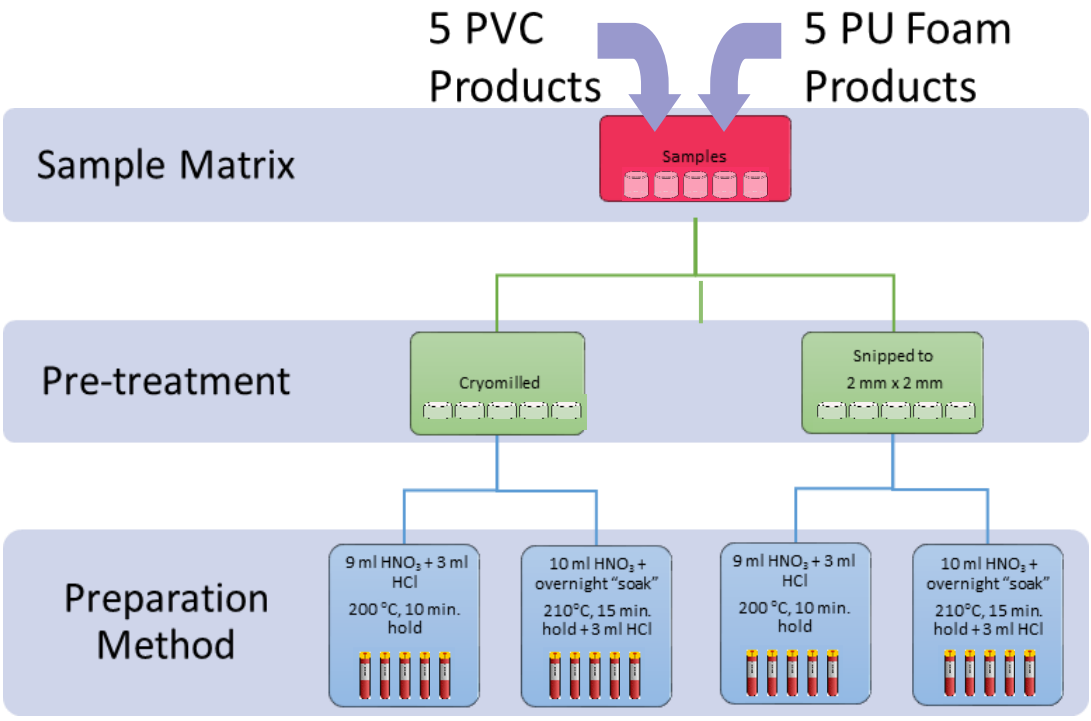

Figure 1. Illustration of the Pre-treatment and Preparation Pathway for Separate Batches of PVC Matrix Samples and PU Foam Matrix Samples.

Samples subjected to the preparation method that combined more nitric acid with an overnight acid "soak", followed by a higher temperature/longer duration microwaving process produced sample aliquots with no to very low amounts of visible residue (Bird, 2015). This indicated a complete to near complete dissolution of matrix and allowed for the analysis method to completely quantitate the level of total mercury of the sample. Techniques to further optimize the methods−including repeating the microwaving step and adding more sample to achieve lower detection limits−were explored. These steps added considerable amount of time to the preparation process, were determined not to further reduce the small amounts of remaining sample residue, and were not useful in lowering the detection limit. These additional techniques were not recommended for the main study. The results of this method development study led the laboratory to recommend that PU and PVC samples be prepared for mercury analysis by the technique employing an overnight acid "soak".

Additionally, it was observed that the samples that were pre-treated with cryomilling achieved a greater occurrence of total dissolution. The cryomilling process produced a fine homogenous powder for both the PVC and PU foam samples, resulting in more complete dissolution. The non-cryomilled (snipped) PU had the most noted residue, regardless of employed preparation method, which was likely due to the snipped foam floating on the top of the acid instead of becoming submerged in the acid prior to the microwave step. Based on the observed results, the recommendation for the main study was to cryomill all the samples. Furthermore, the process of cryomilling also served to better produce homogenous samples for analysis.

Laboratory Procedures

Ecology's Manchester Environmental Laboratory (MEL) cryomilled and processed all study samples using the above-mentioned overnight acid soaking microwave digestion technique (EPA Method 3052 mod.). Analyses were performed on an inductively coupled plasma mass spectrometer (ICP-MS) following EPA Method 6020A. Instruments were calibrated with NIST traceable standards and were verified with a second source NIST traceable standard. All standard residuals and instrument calibration (initial and continuing) verification checks were within acceptance limits.

MEL prepared written case narratives assessing the quality of the data. The written case narratives are available upon request from the study project manager and author of this study.

Data Quality

Quality control (QC) and measurement quality objective (MQOs) criteria are outlined in the QAPP. Upon delivery of the data and case narratives from MEL, the project manager performed a final data review and accepted all data, as qualified.

Method blanks, cryomill rinseate blanks, laboratory control samples (LCS), laboratory duplicates, matrix spikes (MS), MS duplicates and a certified reference material (CRM) were analyzed with each batch of samples. No mercury was detected above the reporting limits (0.010 ppm) in the method blanks or cryomill rinseate blanks associated with each sample batch. All LCS, CRM, laboratory duplicate, MS, and MS duplicate samples met acceptance criteria outlined in the project QAPP.

The CRM included in this study, ERM-EC680k (4.64 ppm mercury) served as an additional consumer matrix-method performance indicator. The CRM, a polyethylene plastic, a similar matrix to PVC and PU, was carried through the same preparation and analysis method as the samples. One CRM sample was analyzed with each sample batch over the course of the study with an average recovery of 103% (n = 16).

Results

A total of 266 product component samples were analyzed by the laboratory for mercury. Fifty-eight product component samples were made from PVC and two-hundred eight product component samples were made of polyurethane (PU) in the form of either plastic (n=53) or foam (n=155). Complete laboratory results for this study can be downloaded from Ecology's Product Testing Database https://fortress.wa.gov/ecy/ptdbpublicreporting/, by selecting Download Data/Study: *Mercury in Polyvinyl Chloride and Polyurethane Novelty and Children's Products.*

Mercury was detected in 11% (30 of 266) laboratory-tested product component samples. From the largest matrix category submitted for testing, PU foam, just over 8%% (13 of 155) of the samples had mercury detections (Table 2). PU plastic, the second polyurethane category, resulted in a 17% (9 of 53) detection frequency. The final matrix category, PVC, resulted in 14% (8 of 58) mercury detections.

Table 2. Summary Statistics of Mercury Detection by Matrix: PVC, Polyurethane (PU) Plastic and PU Foam.

Analyte	PVC	PU Plastic	PU Foam
Number (n)	58	53	155
n > RL	8	9	13
% > RL	14%	17%	8%
Minimum (ppm)*	0.012	0.010	0.014
Maximum (ppm)*	0.030	0.14	0.52

RL= Reporting (quantitation) limit.
RL for EPA 6020A mercury = 0.010 ppm.
** Statistic includes only detected results.*

The highest overall detected level, 0.520 ppm, found in the PU foam sole of an adult slipper. Concentrations of 0.136 ppm and 0.124 ppm were found in a children's belt and bar stool seat cover, respectively. Both of these product components were made of PU plastic, commonly referred to as faux leather on product labeling.

Table 3a. Mercury Detection Summary by Regulating Authority: Mercury Law

Product	Result	Matrix	Category
Slippers	0.520 ppm	PU Foam	Adult Novelty
Bar Stool	0.124 ppm	PU Plastic	Adult Novelty
Red Fashion Belt	0.061 ppm	PU Plastic	Adult Novelty
Storage Ottoman	0.028 ppm	PU Foam	Adult Novelty
Sandals	0.024 ppm	PU Plastic	Adult Novelty
Flip Flops	0.016 ppm	PU Foam	Adult Novelty
Dog Mat	0.014 ppm	PU Foam	Adult Novelty
Round Storage Ottoman	0.013 ppm	PU Plastic	Adult Novelty

Table 3b. Mercury Detection Summary by Regulating Authority: Children's Safe Products Act and Mercury Law

Product	Result	Matrix	Category
Glitter Belt*	0.136 ppm	PU Plastic	Children's Novelty
Fashion Stud Belt	0.118 ppm	PU Plastic	Children's Novelty
Striped Belt (Set with Wallet)	0.087 ppm	PU Plastic	Children's Novelty
Kitten Shoulder Purse	0.080 ppm	PU Foam	Children's Novelty
Black Belt	0.072 ppm	PU Plastic	Children's Novelty
Foam Blocks	0.058 ppm	PU Foam	Children's Novelty
Snow Boots	0.033 ppm	PU Foam	Children's Novelty
Slip and Slide	0.030 ppm	PVC	Children's Novelty
1st Birthday Party Hat	0.026 ppm	PU Foam	Children's Novelty
Belts	0.023 ppm	PVC	Children's Novelty
Glitter Belt*	0.023 ppm	PVC	Children's Novelty
Boxing Gloves	0.021 ppm	PU Foam	Children's Novelty
Starfish Baby Seat Pool toy	0.021 ppm	PVC	Children's Novelty
Toy Dog Vet Kit	0.018 ppm	PU Foam	Children's Novelty
Infant Boots	0.017 ppm	PU Foam	Children's Novelty
Inflatable Linking Pool Tube	0.017 ppm	PVC	Children's Novelty
Foam Blocks	0.016 ppm	PU Foam	Children's Novelty
Mermaid Sirene Doll	0.016 ppm	PVC	Children's Novelty
Sparkling Green Ball	0.012 ppm	PVC	Children's Novelty
Backpack	0.010 ppm	PU Plastic	Children's Novelty

** Inner (PU plastic) and outer (PVC) material of glitter belt.*

Table 3c. Mercury Detection Summary by Regulating Authority: Children's Safe Products Act

Product	Result	Matrix	Category
Step-by-Step Potty Trainer	0.026 ppm	PU Foam	Children's Product
Contoured Changing Pad	0.017 ppm	PVC	Children's Product

Mercury by Regulating Authority

Sixty-five adult-novelty product component samples were submitted for laboratory analysis. The samples included footwear, personal accessories (e.g., belts, purses and hats), and decorative housewares. Mercury was present in just over 12% (8 of 65) of the samples submitted under this category, with concentrations ranging from <0.010 - 0.520 ppm. Tables 3a-c. show mercury detections by matrix and product category.

Many children's products regulated by CSPA are also considered to be a novelty as described by the Mercury Law. In this category (products regulated by both the Mercury Law and CSPA), nearly 11% (20 of 174) of the product samples had detected levels of mercury. Concentrations ranged from <0.010 - 0.136 ppm. Half of these mercury detections were in children's toys or games. Four additional samples were from belts made of PU plastic, accounting for the highest levels of mercury in the category (0.072 –0.0136 ppm). One other belt made from PVC also contained mercury (0.023 ppm).

Products considered to be children's-only products, included items such as baby changing pads, toilet training seats, and car seats. Just over 7% (2 of 27) of the sampled children's-only products showed detections of mercury.

Summary and Conclusions

In 2015, Ecology evaluated novelty and children's products made from, or contained components made from, polyvinyl chloride and polyurethane. Products were collected and tested under the categories of novelty products (adult use), children's products that were also novelty, and children's-only products, based upon descriptions in the Mercury Law and under the Children's Safe Products Act.

Laboratory results from the study indicated the following:

- The highest level of mercury, 0.520 ppm, was detected in an inner PU foam component from a pair of adult slippers.
- Five out of the ten highest concentrations of mercury were found in belts, with concentrations ranging from 0.061– 0.136 ppm. Four of the five were children's belts.
- The pre-treatment and preparation study demonstrated that the pre-treatment technique of cryomilling resulted in less residue in the final sample extracts for the PVC and PU foam samples. Cryomilling samples prior to the preparation method step was selected as the pre-treatment application for the main study. The preparation method technique that produced no to very low amounts visible residue in the processed sample aliquot was selected as the preferred method for the main study.
- As a follow-up to the present study, in the spring of 2016, an additional suite of samples collected as part of this study were submitted for mercury analysis by an alternate analysis method (direct analysis by EPA Method 7473). This project is described in a separate QAPP addendum (Iwenofu, 2016). Results from this work will be reported in a separate technical memo.

Compliance and Enforcement

The laboratory data for this project were submitted to Ecology's Mercury Law and Children's Safe Products Act (CSPA) enforcement coordinators for assessment of compliance with Washington State and Federal laws. Responsible parties (manufacturers, distributors, and/or retailers) of products that appear to violate either law, or have not reported as required by the CSPA reporting rule, are subject to enforcement actions.

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Publication Information

This report is available on the Department of Ecology's website at:
https://fortress.wa.gov/ecy/publications/1603035.html

The Quality Assurance Project Plan for this study is available at:
https://fortress.wa.gov/ecy/publications/SummaryPages/1503106.html

Data for this project are available through Ecology's Product Testing Database at:
https://fortress.wa.gov/ecy/ptdbpublicreporting/
Select Study, *Mercury in Polyvinyl Chloride and Polyurethane Novelty and Children's Products*

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